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REACTIONS BETWEEN COPPER AND CONCENTRATED SULPHURIC ACID.[1]

BY CHAS. BASKERVILLE.

Andrews[2] in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due, not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary product. Having noted frequently the evolution of sulphur dioxide gas before any evidence of this "copper oxide," at the suggestion of Dr. F. P. Venable, I began some experiments with a view of studying this complicated reaction, so simply treated in most text-books.

When my work was completed, in verifying my references I chanced on Pickering's[1] work on the same subject which had escaped me. Most of my work, especially that part which concerns the secondary reactions, is in accord with that of Professor Pickering. My observations concerning the primary reactions were not

1 Read at the Springfield meeting of American Chemical Society.
2 Chem. News, 70, 152: Iowa Acad. of Sciences, Proc. p. 4.

the same however. In making known the latter, I feel at liberty to give the results of my work, as independent corroboration is of some value.

The reactions which take place when copper is treated with concentrated sulphuric acid may be divided into primary and secondary.

Primary:

$$(1)\ Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O.$$

This may be regarded as taking place in two steps:

$$(a)\ Cu+H_2SO_4=CuSO_4+H_2,$$
$$(b)\ H_2+H_2SO_4=SO_2+4H_2O.$$

Still no hydrogen could be detected in the gas given off.

$$(2)\ 5Cu+4H_2SO_4=Cu_2S+3CuSO_4+4H_2O.$$

Secondary:

$$(1)\ Cu_2S+2H_2SO_4=CuS+CuSO_4+SO_2+2H_2O,$$
$$(2)\ CuS+2H_2SO_4=CuSO_4+S+SO_2+2H_2O.$$

The experiments were carried out under various conditions of temperature and time, exposure of the metal to the action of the acid, and varying proportions of metal and acid. The copper ribbon used was cut into small pieces one cm. wide by two to three cm. long. Concentrated c. p. sulphuric acid, 1.84 sp. gr. was used. Each experiment, except where noted, was carried out in a flask in which the air had been displaced by a neutral gas, hydrogen or carbon dioxide. The evolved sulphur dioxide was led through a strong solution of sodium hydroxide and the sulphite formed titrated with a standard iodine solution or oxidized by bromine, and the sulphuric acid determined gravimetrically. A rapid stream of the inert gas was driven through the apparatus just at the close of the experi-

1 J. Lond. Chem. Soc. Trans., 1878. p. 112.

ment. Water was poured into the flask and the whole quickly filtered, and the copper remaining unattacked was then cleaned as well as possible by rubbing, dried and weighed. The copper, as sulphate, was determined by electrolysis. The residue was burned in a porcelain crucible, treated with concentrated nitric acid, ignited and weighed as copper oxide. Sulphur was determined by weighing a dried portion of the residue, treating with carbon disulphide, and the loss in weight taken as sulphur.

Primary Reactions. My experiments showed that the first of the primary reactions predominated when copper was treated with concentrated sulphuric acid at different temperatures (0°–270° C.) At the highest temperature it was found that that reaction alone took place, but at all lower temperatures the second primary reaction also occurred. The proportion of the material following the second equation increased from 0° to 100° C., and then decreased to 270° C., when there was no longer evidence of any such reaction, that is, no black residue was formed.

At the lower temperatures, under 100° C., only the two primary reactions seemed to take place; at the higher temperatures the secondary reactions if the action were prolonged, frequently set in, complicating matters as far as quantitative determinations were concerned. If the time of action were shortened evidence of the occurrence of the primary reactions alone was found. Having an excess of copper present was also necessary, because as soon as all the copper had been attacked the secondary reactions set in at once.

The conditions seemed most favorable for the formation of the insoluble residue at the temperatures from 100° to 130° C. as may be seen from the table. The

proportion of the insoluble residue decreases rapidly in either direction from these temperatures. Some insoluble residue is produced at all the lower temperatures but none is produced when the reaction takes place at 270° C.. and lasts for only a few seconds.

No.	Temperature of reaction.	Copper used.	Copper as sulphate.	Copper as sulphide.	Sulphur dioxide produced.	Ratio of copper sulphate to copper sulphide.
1	0°–10°	0.1350	0.1340	0.0005	0.1343	268.0 : 1
2	"	0.0750	0.0740	0.0003	0.0780	246.0 : 1
3	20°–30°	1.3379	1.3260	0.0121	.....	118.9 : 1
4	"	1.2473	1.2000	0.0184	1.2442	68.0 : 1
5	65°	0 1650	0.1600	0.0050	0.1648	33.0 : 1
6	70°–80°	0.0760	0.0730	0.0035	.....	21.0 : 1
7	100°	0.1380	0.1060	0.0300	0.0840	3.5 : 2
8	"	0.3818	0.2800	0.1082	0.1166	3.5 : 1
9	"	0.9200	0.6400	0.2748	0.2165	3.3 : 1
10	120°–130°	5.2578	4.0800	1.1946	2.0932	3.5 : 1
11	140°–160°	5.0900	4.5100	0.5759	3.3084	8.0 : 1
12	160°–190°	1.1375	1.1200	0.0930	.....	12.0 : 1
13	200°–220°	1.5450	1.4518	0.0932	1.0904	16-0 : 1
14	220°–230°	0.9815	0.9400	0.0332	0.9365	29.0 : 1
15	230°	3.8915	3.8200	0.0796	3.6327	49.0 : 1
16	230°	2.0000	1.9750	0.0388	2.2313	51.0 : 1
17	240°	1.1235	1.1035	0.0200	0.9855	55.0 : 1
18	250°–260°	2.1365	2.1000	0.0280	2.0304	80.0 : 1
19	270°	4.0000	.....	None.	.....	....

Berzelius[1] noted this black substance when copper was treated with concentrated sulphuric acid. He said it appeared to be a subsulphate because it was oxidizable by nitric acid. He made no quantitative determinations to show its composition. Such a body would contain fifty-seven per cent. of copper and in no case did I find the black residue to contain less than 67.64 per cent.

Barruel[2] found that sulphuric acid acted on copper at ordinary temperatures if sufficient time were given. He claimed that the sulphur dioxide produced was dissolved in the acid and attacked the copper forming cop-

1 Traite de chimie 4. 324.
2 Journ. de Pharm. 20. 13. 1834.

persulphide and oxide, the latter being dissolved in the acid.

Maumené[1] claimed that his black residue contained four different bodies; copper subsulphide and three oxysulphides, $CuO.2Cu_2S$ or Cu_5S_2O, $CuO.2CuS$ or Cu_3S_2O, and $CuO.CuS$ or Cu_2SO.

In my analyses, as also in Pickering's, the sum of the percentages of copper and sulphur always approximated 100. In one experiment I did find a body whose composition approximated $CuO.2Cu_2S$. I shall speak of that apparent exception further on.

Calvert and Johnson[2] performed some experiments on the action of strong and dilute sulphuric acid on copper at temperatures from 130° to 150° C. They noted the formation of the subsulphide and claimed it was due to the liberation of free sulphur which afterwards combined with the copper direct.[3] There was evidently something very wrong in their observations, for they failed to note any action below 130° C. Barruel in 1834 had noted that action took place at the temperature of the air. I have noted the action at 0° C.

According to Andrews

$$Cu+SO_3=CuO+SO_2$$
$$CuO+H_2SO_4=CuSO_4+H_2O$$

are the correct formulas, SO_3 existing at the temperature necessary for the reaction, and the insoluble residue being the oxide. That would do if the reaction occurred only at those higher temperatures, whereas it occurs as well at 0° C. Besides this the undissolved residue is not the oxide at all, as he says it is, but

1 Ann. Chim. Phys., 1846, 3rd Series, 18, 311; Traite de chimie generale, Pelouze et Fremy, 2nd Ed., I, 388.

2 J. Chem. Soc., 19, 438, 1866.

3 Pickering proved this impossible. The amount of sulphide produced was not increased by adding sulphur direct to the experiment.

invariably the sulphide. In making his analyses very likely he determined the copper alone and the percentage of copper in copper oxide and cuprous sulphide is the same. In a subsequent conversation with Dr. Andrews, I haved learned that this was the case. This black residue when thoroughly washed free from any sulphuric acid always gave off hydrogen sulphide on treatment with hydrochloric acid.

The composition of the insoluble residue was determined by analysis:

	Found.		Calculated for Cu_2S.
Sulphur.....	20.44		20.14
Copper.....	79.56	(by difference)	79.86
	100.00		100.00

In the first of the two primary reactions,

$$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O,$$

it is seen that for each atom of copper found as sulphate, one molecule of sulphur dioxide should be evolved. Calculating on this basis from the following table we have the ratio of 2 : 3 between the copper as subsulphide and the copper as sulphate unaccounted for in the production of the sulphur dioxide.

No.	Sulphur dioxide.	Corresponding copper.	Total copper as sulphate.	Copper as subsulphide.	Difference. Columns 3 and 4.	Ratio. Columns 5 and 6.
8	0.1166	0.1158	0.2800	0.1082	0.1642	2 : 3
9	0.2165	0.2132	0.6400	0.2758	0.4268	2 : 3

The formula

$$5Cu+4H_2SO_4=3CuSO_4+Cu_2S+4H_2O$$

shows that relation between the two compounds of copper.[1]

Second Reactions.—The secondary reactions depend

1 Pickering states (loc. cit., p. 117) that once at 80° C. he observed that the copper in the two compounds stood in the relation of 2:2.9. I have not been able, however, to have concentrated sulphuric acid act on copper at any temperature from 0° C. to 270° C. without the evolution of sulphur dioxide, which is not accounted for at all in case the second of the primary reactions alone takes place, which he states did take place at 80° C.

upon the second of the primary, that is, the cuprous sulphide produced. If the experiment were carried out so as to cause a rapid evolution of gas and the residue not allowed to form a protective coating over the copper, as long as an excess of the metal was present, only the primary reactions occurred. This was accomplished at 160°–170° C. If the strips of copper were touching they almost always became bound together by the anhydrous copper sulphate and a coating of the black residue formed a protective covering to the copper. When such a state of affairs occurred, no sharply defined line could be drawn to show, of these secondary reactions, when the first ends and the second begins, because as soon as some cuprous sulphide is changed to cupric sulphide, the latter is attacked by the sulphuric acid, sulphur being one of the products of the last reaction. Several experiments carried out at 140°–150°C. when this occurred with an excess of copper gave evidence of all the reactions, primary and secondary. Sulphur was deposited on the sides of the flask and the black residue contained 20.71 per cent. sulphur, and the theoretical percentage for cuprous sulphide is 20.138. This showed the presence of some cupric sulphide in which the percentage of sulphur is 33.59[2].

Some freshly prepared cuprous sulphide was treated with concentrated sulphuric acid. Sulphur was determined in the undissolved residue, the free sulphur being first removed.

	Found.	Calculated for CuS.
Sulphur.....	32.36	33.59

The formula,

2. Watts (vol. II, p. 41, 1875, Ed.) notes this complete decomposition.

$$Cu_2S+2H_2SO_4=CuS+CuSO_4+SO_2+H_2O$$

explains such a change.

Another portion of cuprous sulphide was boiled with concentrated acid until it nearly all disappeared. The free sulphur produced was determined.

	Found.	Calculated.
Sulphur.....	19.71	20.138

The formula

$$Cu_2S+4H_2SO_4=2CuSO_4+2SO_2+S+4H_2O$$

shows the final result of the continued action of sulphuric acid on the subsulphide.

From these data the secondary reactions between copper and concentrated sulphuric acid may be expressed by the two formulas,

1. $Cu_2S+2H_2SO_4=CuS+CuSO_4+SO_2+2H_2O$.
2. $CuS+2H_2SO_4=S+CuSO_4+SO_2+2H_2O$.

The occurrence of sulphur on the sides of the flask at the end of the reaction may be said to be due to the sublimation of that element which is produced by the direct decomposition of sulphuric acid without the intermediate formation of hydrogen sulphide for the following reasons:

1. If hydrogen sulphide were produced by the decomposition of the sulphide, it is natural to expect some to escape in the gases which are given off. None could be detected.

2. As is well known, hydrogen sulphide is decomposed by concentrated sulphuric acid.

3. The deposit of sulphur is first noted on the sides of the flask and not in the delivery tube where the gases, hydrogen sulphide, and sulphur dioxide, would naturally come into the most intimate relations.

4. If flowers of sulphur be heated with concentrated

sulphuric acid in a flask provided with a long outlet tube, much of the sulphur will be seen to creep up the sides of the flask, and some sublimed even into the tube, which shows that the state of affairs observed may be attained without any trace of hydrogen sulphide being present.

COPPER OXYSULPHIDE.

Contradictory evidence to what has been stated above was found in one case where the insoluble residue approximated $CuO.2Cu_2S$ in composition. This is one of the oxysulphides stated by Maumené to exist in the black residue. The acid was heated to 250° C. in an Erlenmeyer flask. The air was not removed by an inert gas. The copper was suspended in long strips, only a third of which was immersed in the acid, the other part being exposed to the air.

The black residue formed under these conditions gave on analysis:

	Found.	Calculated for $CuO.2Cu_2S$.
Sulphur	16.16	16.15
Oxygen	3.54	4.03
Copper	undetermined	79.82

Schuster[1] found that copper was acted on by dilute sulphuric acid only in the presence of atmospheric oxygen. Traube[2] noted that copper was not oxidized in moist air, but was slowly in the presence of dilute sulphuric acid. Although copper is unable to decompose sulphuric acid at ordinary temperatures (according to Traube) its affinity for SO_4 and that of hydrogen for oxygen are together sufficient to cause such a decomposition, the probable reaction being:

1 Proc. Roy. Soc. 55, 84; Ber. d. chem. Ges., 28, 219.
2 Ber. d. chem. Ges., 18, 1887-1890.
3 Loc. cit., p. 138.

$$Cu+H_2SO_4+O_2=CuSO_4+H_2O_2,$$
and $$CuH_2O_2=CuO+H_2O.$$

I could detect no oxygen in the gases given off when the experiments were carried out in an inert atmosphere. Nor could I detect hydrogen dioxide. Traube himself states that no "active" oxygen was liberated in the reaction because carbon monoxide was not oxidized to carbon dioxide. Pickering[3] suggests that the sulphide formed is "oxidized at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas."

UNIVERSITY OF NORTH CAROLINA.

SOME OF THE PROPERTIES OF CALCIUM CARBIDE.

BY F. P. VENABLE AND THOMAS CLARKE.

The calcium carbide used was prepared by the Wilson Aluminum Company. In this preparation, lime is mixed with some form of carbon, as coal-tar; the mass is then heated, with stirring, until a thorough mixture is obtained. The proportions are so arranged that the mass becomes dry and hard on cooling. This mass, in lumps, is then placed in the electric furnace. In a very short time after the turning on of the current, the process is complete. The molten mass can be run out of the crucible or it may be removed after cooling. On examination, it is easy to see that there is more or less carbon unchanged, or rather converted into the graph-

itic variety by the intense heat. Along with this are to be seen crystalline masses, lustrous and dark brownish black in color.

These are quite hard, and break with a crystalline fracture. Several efforts at effecting a separation from the graphitic carbon were unsuccessful. The lustre is slowly lost on exposure to air, more rapidly if the air be filled with moisture. The work will finally crumble down into a gray powder with particles of black graphite interspersed through it. The carbide can be kept for a year or two if placed in a tightly stoppered bottle and is quite easily preserved if a little coal-oil is placed in the vessel containing it.

By far the most interesting property of this carbide is its decomposition when brought in eontact with water. The metallic carbides seem to be distinguished by the ease with which they exchange their carbon for the oxygen of water or for the radicals of various acids, the carbon combining with the hydrogen to form various hydrocarbons. Several authors have reported that the decomposition of this particular hydrocarbon caused the formation of acetylene. Experiments were carried out by us proving this fact, some time before there were any publications concerning it in the chemical journals, but we were not at liberty to publish anything concerning it at that time. If the gas, as evolved, is passed through a set of absorption flasks containing ammoniacal copper solution it will be entirely absorbed, not a bubble passing through, out of one or two liters of gas. Thus it seems to be pure acetylene. The amount of gas yielded by any one sample will be affected to some extent by the amount of graphitic carbon present. Hence different lots will vary some-

what. The average is about 200 cc. to the gram of carbide.

If the gas be ignited, as it is evolved, it gives a smoky flame; if it be considerably diluted, as one part of gas to from six to ten of air, a flame of great brilliancy and intensity is gotten. A company has been formed to introduce this as an illuminant upon the market. The cheapness of the materials used and the ease with which the gas can be found ought to make it a valuable and useful addition to our illuminants. If too large a proportion of air be admixed a very violent explosion can be brought about by igniting it. In some cases we have noticed the flame rapidly travelling backwards along a rubber tube towards the gasometer in which the gas was stored. One explosion taught us that care was necessary in handling the mixture.

Several analyses were attempted of the carbide, but for obvious reasons failed to give very satisfactory results. In the first place there was uncombined carbon present, also a small portion of a tarry matter, which could be detected by heating to high temperatures, and lastly, the specimens worked upon were several months old and in spite of careful keeping, had been slightly acted upon by the air and so contained uncombined lime or calcium carbonate. Moissan gives C_2Ca as the formula calculated from his analyses. This would agree well with the decomposition by water;

$$C_2Ca+HO_2=C_2H_2+CaO.$$

Action of Hydrogen upon the Carbide.—Dry hydrogen has no action upon this carbide in the cold. Several small pieces of the carbide were placed in a piece of combustion tubing, drawn out at one end to a point suitable for testing the flame. Dry hydrogen was then passed over it and as soon as the air was expelled the

hydrogen was ignited at the jet and a lamp placed under the tube so as to heat the carbide. In a little while the colorless flame became luminous and remained so a short time. A brownish, tarry matter condensed in the cooler parts of the tube. The mass of the carbide assumed a dull grey tint and a very thin white sublimate collected at a short distance from where the tube was heated. The ignition was carried on for five hours. The driving off of this tarry matter seemed to be the only action. The substance on removal from the tube, was still hard. On exposure to the air, it disintegrated, and, if thrown into the water, it was decomposed, showing the same behavior as the original carbide.

Action of Air and of Oxygen.—Some fresh pieces of the carbide were placed in the tube and heated while dry air was passed over them. A luminous flame was gotten as before and the same tarry matter was driven off and then there seemed to be no further action. Tests showed the carbide apparently unchanged at the end of prolonged heating.

Oxygen was then passed over some of the carbide which was being moderately ignited. No change was observed after two hour's heating. If the temperature was very high, such as that gotten in a combustion furnace, the carbide glowed brightly, as if burning, and a nearly white powder was obtained. The combustion was imperfect, however, unless the tube was very hot and the ignition prolonged. This refers not merely to the graphitic carbon mixed with the carbide but to the carbide itself. In several experiments the substance withdrawn from the tube, after heating some hours in oxygen, decomposed violently in water. It may be added, as was to be expected, that carbon dioxide had no appreciable action upon the carbide.

Action of Hydrochloric Acid.—Hydrochloric acid had no action upon this substance in the cold. When passed over the heated substance it caused it to swell up and assume a dirty gray appearance. A small amount of a liquid, apparently water, collected in the cooler portions of the tube and parts of the carbide fused down in glassy globules and masses. These were soluble in water and were easily shown to be calcium chloride. White fumes were evolved, some of which settled as a white solid upon the sides of the tube.

Action of Chlorine and Bromine.—When chlorine was passed over fresh carbide in the cold no action was observed. If even a moderate heat was applied, however, the lumps of carbide glowed very brightly, swelled, and fused together. A slight yellowish white sublimate was found in the tube. The fused mass was calcium carbide.

Bromine mixed with air was then passed over the fresh carbide. In the cold no action was observed. On heating, the carbide became red and the smaller pieces glowed. The lumps fused together and bubbles were observed on the surface as if some gas was escaping from the mass. Some condensed matter was found afterwards in the tube, and, on cooling, a peculiar odor was noticed different from that of the bromine. The fused mass dissolved readily in water and gave the tests for calcium bromide. Of course in this and the previous experiment the black specks of graphitic carbon were found unchanged. It was easy to distinguish them from the carbide. A few pieces of the carbide were dropped into strong, freshly prepared, chlorine water. There was a very violent disengagement of gas but it was not ignited as reported by Moissan. The gas was inflammable and burnt very much like acety-

lene. The odor was, however, peculiar. The same experiment was tried several times with a concentrated solution of bromine in water. The action again was very violent but there was no spontaneous ignition of the gas. Little difference could be detected between this and the action of the chlorine water.

Action of Acids.—A piece of the carbide was placed in concentrated pure sulphuric acid. A few small bubbles came off but the action seemed light. On heating, the action was greatly increased and continued after the removal of the flame. A gas was given off which burned with a luminous flame.

A mixture of sulphuric acid and potassium bichromate acted most violently upon the carbide. There seemed to be a very vigorous oxidation, and several attempts at igniting the gas given off resulted in failure. There could have been very little, if any, acetylene present in it.

Strong nitric acid attacked the carbide with the formation of brown-red fumes. The gas evolved could be ignited and burned with a smoky flame.

Glacial acetic acid decomposed the carbide slowly in the cold.

It may be added that no change was observed on adding a piece of the carbide to some boiling sulphur. On allowing the mass to cool the carbide was regained in its original condition.

Action of Alkalies.—A few grams of sodium hydroxide were melted in a nickel dish and a piece of the carbide was added. There was violent action, a gas being given off which burned with a luminous flame and which was taken to be acetylene.

A small amount of sodium dioxide was also melted in a nickel dish. When the carbide was added to this

it was rapidly attacked, the action being about the same as in the experiment just mentioned. An inflammable gas was evolved.

In conclusion, we would give due credit to Mr. W. R. Kenan, who carefully verified some of the experiments here recorded.

UNIVERSITY OF NORTH CAROLINA.
February, 1895.

ZIRCONIUM SULPHITE.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Very little is recorded in the text-books on chemistry with regard to this compound of zirconium. Berthier is reported as having examined it and found it to be a white insoluble body, slightly soluble, however, in an aqueous solution of sulphurous acid, from which it is thrown down again upon boiling. Whether this was what is commonly known as the neutral, or the acid, or a basic sulphite, is not recorded. It is highly probable that with so weak an acid as sulphurous acid, zirconium would form under these circumstances only basic compounds. We may state with regard to our own work that we have been unable with one exception to form any sulphite corresponding to the acid or the neutral. Only very indefinite compounds or mixtures of the sulphite with the hydroxide have come into our hands, as a rule.

The subject was first brought to our attention by the study of the reaction utilized by Baskerville for the quantitative separation of zirconium from iron and

aluminum.[1] It was also put into use by him for shortening the method of preparing the pure zirconium chlorides.[2] The reaction in question is that which takes place when a nearly neutral solution of zirconium chloride is boiled with sulphur dioxide in excess.

Several points of interest were observed as to this reaction. It was found that when a solution of the sulphate was used it was difficult to secure any precipitation by means of sulphur dioxide even with persistent boiling. The chloride was clearly the best salt to use. The pure chloride was made up into approximately a two and a half per cent. solution and this was either very nearly neutralized by means of ammonia, or ammonia was added until there was a slight permanent precipitate. In the latter case the saturation of this solution with sulphur dioxide produced an immediate precipitate. If this were permitted to stand for some time the precipitate was redissolved, the remaining liquid being only slightly clouded. This re-solution was probably due to the hydrochloric acid liberated and also to the excess of sulphurous acid present. If this solution of zirconium chloride saturated with sulphur dioxide were diluted with several times its volume of water and boiled from fifteen to thirty minutes, a heavy white precipitate was produced. This was quite easily filtered by means of an unglazed porcelain suction filter. The precipitate was washed several times and finally dried over sulphuric acid in a desiccator. The analysis gave:

Zirconium dioxide...	61:10	61:75	61:75	....	61.00	....	....
Sulphur dioxide.....	....	....	....	....	....	22.24	22.20

Ratio of zirconium to sulphur dioxide is 2 : 1, approximately.

Ratio of zirconium to sulphur dioxide in the neutral sulphite, $Zr(SO_2)_2$, is 1 : 1.4.

1. J. Am. C. Soc. 16. 475.
2. This Journal, 11. 85.

This substance when so dried was perfectly white and quite hard. It was powdered with some difficulty in an agate mortar and resembled, very much, finely divided silica.

It was sometimes noted that the precipitate formed on passing the sulphur dioxide into the solution of zirconium chloride was partially dissolved upon the prolonged passage of the gas. To determine in how far the liberated hydrochloric acid was the agent causing this re-solution, some zirconium hydroxide, freshly precipitated by means of ammonium hydroxide, was washed free from hydrochloric acid and was then treated with a concentrated and freshly prepared solution of sulphur dioxide. This was allowed to stand during two or three months and was frequently shaken. The solid at the bottom of the flask separated into two layers, the gelatinous hydroxide settling first and upon this a white, finely divided, substance formed. The supernatant liquid was found to contain zirconium. The white layer was separated from the hydroxide and analyzed. It contained:

Zirconium dioxide	15.05	15.53	....
Sulphur dioxide	....	....	4.86
Water (blast-lamp)	2.78	3.03	....
Water, at 95° C	77.41	76.33	....
	100.10	99.75	

Ratio of zirconium to sulphur dioxide is 2.2 : 1.

This substance apparently came to a constant weight on drying in a steam-bath at 95° C.

A somewhat peculiar product was obtained during an attempt at filtering the precipitated sulphite. It filtered very slowly and in the course of a few hours a layer of a watery liquid formed above the white sulphite. This was allowed to stand several days and turned into a solid jelly. This was noticed several

times. The thickness of the jelly-like layer, would of course, depend upon the amount of moisture in the precipitate but several times it was half an inch or more in thickness. This body was analyzed in the moist condition after simply drying between filter paper. It gave:

Zirconium dioxide.....	20.02	20.65	....	....
Sulphur dioxide.....	....	....	5.19	5.51
Water (blast lamp).....	9.14	8.53	....	....
Water, at 95° C.....	65.65	65.22	....	....
	100.00	99.91		

Ratio of zirconium and sulphur dioxide is here 3 : 1.

A portion of this jelly was brought to constant weight by heating for a number of hours in a steam-bath. About sixty-five per cent. of the original weight was lost and the body assumed a translucent appearance like dried gelatine. The analysis of this gave:

Zirconium dioxide.....	59.34	....
Sulphur dioxide.....	....	11.46
Water (blast-lamp)	29.20	....
	100.00	

Ratio of zirconium to sulphur dioxide is 4 : 1.

The analysis shows that some of the sulphur dioxide was lost on drying.

It will be seen that these different preparations show a very varying ratio of the zirconium to the sulphur dioxide and in no case approach to the ratio of the neutral sulphite (1 : 1.4). They are, therefore, to be looked upon as either mixtures of the sulphite and hydroxide or very unstable compounds. The jelly-like substance mentioned last gives more promise of being a chemical individual; still it has not been thought legitimate to attempt the calculation or assignment of a formula to it.

A last attempt at preparing the neutral sulphite was made by placing some of the excess of sulphurous acid,

which had been standing over the precipitated zirconium sulphite, in a dessiccator and allowing it to evaporate over sulphuric acid. The bulk of liquid decreased from about 200 cc. to five to ten cc. and then hard, white, warty crystals began to form, which were quite difficult to remove from the crystallizing dish. In appearance they resembled zirconium sulphate. The solution had lost the odor of sulphur dioxide. The time consumed in the evaporation was several months.

The crystals were dried upon filter-paper and yielded, on analysis:

Zirconium .....24.47 per cent. on a dry basis, 36.43.
Sulphur dioxide 34.54 " " " " " 51.42.

Calculated for $Zr(SO_3)_2$, Zr 36.25; SO_2 51.20. These crystals then seemed to be a hydrated sulphite of the composition $Zr(SO_3)_2\ 7H_2O$.

The nature of the precipitate gotten by means of sodium sulphite was also examined. The sulphite used was fairly pure. The zirconium chloride solution was distinctly acid and the mixed solution was acid. A transient precipitate was produced in the cold on mixing the two. On heating, a good flocculent precipitate was formed which settled well and was easily filtered. The precipitate looked like the hydroxide, rather than the white sulphite already described. The analysis gave:

Zirconium dioxide.....	5.75	5.75	....	....
Sulphur dioxide	....	....	1.05	1.004

Ratio of zirconium and sulphur dioxide is 4 : 1.

Chancel,[1] in giving a method of separation of iron from zirconium, states that by means of a boiling solution of sodium thiosulphite the zirconium is precipitated as thiosulphite. Stromeyer[1] stated that if a dilute

1 Ann. d. Chem. u. Pharm., 108, 237; Watt's Dictionary, 5, 1081, 1877.
1 Ibid. 113, 127.

zirconium chloride solution be neutralized by sodium carbonate in the cold and sodium thiosulphite added until the solution was decolorized and then boiled as long as sulphur dioxide came off, the zirconium would be precipitated as oxide (meaning doubtless hydroxide).

To test these observations a solution of zirconium chloride was neutralized by ammonia and an excess of sodium thiosulphite was added in crystals. A precipitate began to be formed directly. This was washed eight or ten times by decantation, filtered, the precipitate dried by absorption paper, and analyzed. It gave:

Zirconium dioxide.....	19.66	20.50	....	....
Sulphur dioxide.....	....	....	4.03	4.14
Water (blast-lamp).....	16.05	16.41	....	....
Water, at 95° C....	60.11	58.58	....	....
	99.85	99.61		

Percentage of zirconium on a water-free basis is 75.
Percentage of zirconium calculated in $Zr(S_2O_3)_2$ is 21.95.

A second experiment was carried out with an acid solution of zirconium chloride. The sodium thiosulphite crystals were added in the cold and when completely dissolved the solution was heated to boiling. This precipitate, on analysis, gave:

Zirconium dioxide	21.74	20.73	....	....
Sulphur dioxide.....	....	....	5.33	5.41
Water (blast-lamp).....	9.72	8.64	....	....
Water, at 95° C.....	63.28	65.37	....	....
	100.07	100.15		

Finally another portion was taken, precipitated with an excess of sodium thiosulphite, and boiled until there was no longer any odor of sulphur dioxide. This precipitate was analyzed:

Zirconium dioxide... ..	47.01	47.19	....	....
Sulphur dioxide.....	....	....	6.90	6.95
Water (blast-lamp).....	21.41	21.14	....	....
Water, at 95° C....	24.16	24.72	....	....
	99.48	100.01		

The percentage of water here was due to the exposure of the precipitate in a warm room and its consequent partial drying. There is no evidence here nor in the previous cases of the formation of any definite thiosulphite and we would question its existence under ordinary conditions. There is no evidence of the formation here of an hydroxide as one of the authors quoted states. Basic salts seem to be the only products.

UNIVERSITY OF NORTH CAROLINA,
March. 1895.

THE CHLORIDES OF ZIRCONIUM.

BY F. P. VENABLE.

In a report upon the examination of the chlorides of zirconium[1] it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallization from the concentrated acid. This statement was based on a partial analysis by Linnemann[2], the result of which made him call the substance the tetrachloride; and on repeated partial analyses of my own, in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agree-determinations were made and they yielded as the percentage of zirconium dioxide found 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey)

1. J. Am. Chem. Soc. 1894. 16. 460-475.
2. Lond. Chem. News. 52. 233-240.

39.16 per cent. of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body and considered it the oxychloride. His determinations varied so greatly and his mode of drying were so faulty that I simply concluded he was mistaken, being unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent. of zirconium to 46.79 per cent., the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product and was greatly surprised to find only 35.5 per cent. of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation and the constancy of its composition, along with its stability, would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is $Zr_3(OH)_6Cl_7\ 5H_2O$.

UNIVERSITY OF NORTH CAROLINA.
August, 1895.

THE DRUDGERY OF SCIENCE.

The study of Natural Science presents so much that is attractive and entertaining that a distaste is some times begotten in the mind of the beginner for the sober, plodding side of it. A lecturer upon Geology

or Chemistry is at the disadvantage of having an audience which expects to be amused, as at some exhibition of jugglery, whereas the language teacher has under him those who realize fully that there is no royal road to learning. I have heard a distinguished professor of chemistry say that he always felt his class begin to drag when he passed the "fizz, pop and bang stage." They would gaze in wonder at the beautiful experiments upon the elemental gases but had no stomach for the hard work of the science. And yet, how essential this plodding, this toil without apparent, or at least immediate, reward, is to the truth of the picture and to the success of the study. The drudgery ceases to be such in the eyes of the enthusiastic searcher into nature's mysteries. It becomes a joy, as bringing him a step nearer to the realization of his hopes.

If any of you are looking forward to a life-time of work in the realms of science it is well that you should face clearly the condition demanded of you for the highest, truest success, namely, patient and often times seemingly fruitless toil. A patient worker who has just laid his tribute on the altar of science, before an admiring world of fellow-citizens—I refer to Morley and his monumental work upon the atomic weight of oxygen—writes:

"Do not deceive yourselves, however, by thinking that patient toil can accomplish everything. Genius is not 'an infinite capacity for taking pains' but a something broader and deeper, that lifts the drudgery into the sublime. You may take infinite pains and still be only a drudge. You must take infinite pains to be a brilliant leader."

One of the most valuable qualities of mind to a man of science is persistence, obstinacy, doggedness—what-

ever you may choose to call it. It means an unyielding determination to persevere in spite of difficulties and discouragements. Accuracy of observation, clearness of intellect are all good and necessary, but unless you have genuine grit, and stick at the task you have set yourself, you can make no very valuable conquest from nature nor contribution to the store of human knowledge. It is the patient settler who has cleared the land, tilled the soil, sown the seed, toiled, suffered and waited and thus has won for the world its great feeding-ground in our Western States, and so it is the patient Darwin, the toiling Agassiz, the untiring Liebig, who have opened to us such great vistas in the domain of science. If we would follow them we must toil over the stepping stones they have succeeded in laying. If we would go yet further and discover Nature's secrets for ourselves, a capacity for patient drudgery must be ours. And yet, though it seem drudgery to others who are merely looking on, it is not really such, for to us it must be a labor of love.

I wish to bring before you some eminent examples of drudges that you may draw encouragement from them. Many instances might be drawn, first, from the life of Darwin. Take, for example, his patience when he reports himself as watching for two hours to see whether a spider put the right foot or the left foot in front in weaving, and his honesty in confessing, at the end of it, that he could not tell. Consider those fifty years during which he watched the lowly earth worm and found out for us its beneficent action in preparing our soils.

Patient drudges, or shall we call them heroes, are to be found in all the branches of science. Think of Lubbock and his work with ants and bees; of Ehrenberg

and his blinding himself with his microscopic investigation of infusorial earths; of Galileo and his telescope. My acquaintance lies mostly, however, with chemists, and I shall draw from among them the examples we need.

Some years ago Dr. Kerr, our former State Geologist, supplied a distinguished English chemist, Dr. Crookes, with a large amount of a rare mineral, samarskite, found in this State. Years were spent by this gentleman in, what he speaks of as the most trying and laborious of work, fractional precipitations, in order to separate the rare elements contained in the mineral. This meant a repetition for many hundreds of times of the same delicate and trying operations. The final report of the work occupied only a few pages and gave to the uninitiated little sign of the labor spent upon it.

Another instance of the same sort of work came to my notice a few years ago. Dr. Shapleigh, an ambitious American chemist, wrote me that he too had been working on the rare earths (from cerite and monazite also gotten from this State) trying to separate praseo- and neo-dymium and to prepare their compounds, with the hope of thoroughly studying them. After three years of daily toil and over 400 precipitations from 8 or 10 tons of materials, he had them separated and the compounds prepared and then found himself unable to continue the work and earn the reputation which he so richly merited.

A German chemist wishing to find out some of the constituents of the sugar-beet worked over six thousand pounds of them in small portions, by prolonged and patient operations.

We have some remarkable instances of patient toil among the older chemists also. Thus Boerhaave dis-

tilled the same lot of mercury five-hundred times to contradict the old alchemical notion that an essence could be gotten from it, and other mercury he kept at a raised temperature for fifteen years, watching for any changes, meaning countless repetitions of the same tiresome work.

I knew, myself, a young German student who, for weeks and weeks, was practically an outcast, working in a part of the laboratory to himself, unable to eat with his fellows, a burden to himself and to others because of the loathsome chemical substances he had chosen to work upon. We always threatened to put him under the sink or soak him in the water butt if he came near our part of the laboratory, and so I know little of his work or success, but he showed the scientific spirit and pluck. The work had to be done to gain the desired knowledge. It was loathsome, it was drudgery, but someone had to do it, and why not he?

I have heard of an American student who spent months in distilling and examining foetid bone oil. It seems to me, as a would-be scientific man, I should be forced to draw the line at bone-oil.

Only a year or two ago, I reported to the Society the patient toil of an English worker who was trying to understand the processes in the germination of grain. His microscopic dissections counted up into the hundreds, and yet, though spoken of casually and as a matter of course, seemed to me a marvellous proof of skill and patience.

But this drudgery may meet you at the outset of your career, and not only after you have become veterans, and if we listen to the older masters of Science, it is best for us that we should be so tried.

My teacher was one of the pupils of the great Ger-

man chemist Wöhler. He told me that when he first entered Wöhler's laboratory, the dried-up looking but brilliant German set him to grinding some hard substance in a mortar, and kept him at that and nothing else for three solid weeks. Perhaps it was the memory of this that made him set me, first, at a task of distilling water and keep me watching its drip, drip, for one long and weary week.

How such training can be of use, is told us in the charming and all too short autobiography of Justus v. Liebig, published by the German Chemical Society. His father was a dealer in colors. The boy, driven by the workings of the chemist spirit within him, experimented with his father's slender store of chemicals, and as the possible mixings and changes were necessarily limited, never wearied of repeating them, learning thus exactly the appearance and the changes they underwent, and acquiring perfected powers of observation to which he largely owed his after successes. He says, that it taught him especially to detect without fail similarities between bodies. Wöhler's training led him to take the contrary view and always to see the differences between the different kinds of matter before him. As much of their work was done in common, these two great men supplemented one another in their trained faculties, and from the farmer to the manufacturer, from the poor man who enjoys cheap clothing and better food to the suffering patient who is restored to health, mankind arises and calls them blessed.

Please note that this toil and drudgery is something different from the hap-hazard work of the alchemists and gold-seekers of the middle ages, and yet all of you have heard the tales that go to show how all-consuming was the pursuit of that flighty, illogical work.

That which I have been referring to is logical, carefully planned work, with definite ends in view.

I will close by recounting for you, in part, the story of Palissy, the potter. It may be a twice-told tale to you, but it well illustrates scientific drudgery pursued either to death or to success. Europe was without porcelain. The only pottery known to French art was common earthenware. Palissy set for himself the task of discovering how the beautiful enamel was made which could be seen on priceless ancient pieces or on imported Eastern ware.

How was he to begin? He had no teacher, he had no property. He himself says:

"Without having heard of what materials the said vessels were composed, I pounded, in those days, all the substances which I could suppose likely to make anything,and having pounded and ground them I bought a quantity of earthen pots and broke them to pieces. I put on them some of the materials that I had ground and having marked them, I set apart in writing what things I had put upon each, and having made a furnace to my fancy, I set the fragments down to bake."

He built his furnaces, exhausted his resources and *failed.* He pulled down his furnaces, broke fresh pots, undeterred by an empty purse, an empty cupboard and a remonstrating wife, and *failed again.* Then he prepared three or four hundred pieces and sent them to a neighboring potters-kiln to be burned, after, as he says, he "had fooled away several years, with sorrows and sighs because he could not arrive at his intention." The result was that he "received nothing but shame and loss because they turned out good for nothing." This he did several times with failure only for his reward. Then hunger at home and the clamors of Mad-

ame Palissy could no longer be disregarded and he gave up for awhile.

For a year and a half he was conjugally a happy man, but scientifically wretched, for the fire of genius within could not be quieted. Having earned some little money by other work, he turned again to his enamel. For two years he continued his experiments and Madam Palissy scolded. His house was stripped, his children hungry. He agreed to make one final experiment, and if it failed to give up that for which he had labored five long, hard years. His trial was a partial success and nerved him to further efforts.

Time fails me to follow him through all of his trials and disappointments. I do not know of any more pitiful and yet more wonderful and stirring account of man's triumph over obstacles that most would call insurmountable.

He blundered thus for fifteen or eighteen years. He wasted away until there was no form nor prominence of muscle on arms or legs. He received no help nor consolation at home nor abroad, and yet he triumphed at last. The secret was learned, the art was won. Noblemen visited his cottage. Madame Palissy smiled again and purchased a "fine grass-green camlet" as some sort of amends for her furniture, burned in his furnace, and her years of home happiness sacrificed. He removed to court, was highly fav oredby the king, and France and Europe were filled with his fame.

May you have something of his energy and his perseverance and be blessed with wives more patient and more helpful than Madame Palissy.

NOTES ON THE UNDERGROUND SUPPLIES OF POTABLE WATERS IN THE SOUTH ATLANTIC PIEDMONT PLATEAU.*

BY J. A. HOLMES.

It is a fact that is coming to be more widely recognized by the general public as well as by members of the medical fraternity, that the health of persons living in our hill country depends in no small degree upon the drinking water obtained,—just as it has been found that the use of pure water in the lowlands and swamp areas of the Southern states results in practical immunity from malarial diseases. Hence the problem of how to obtain supplies of wholesome water for the towns and manufacturing establishments in the hill country or Piedmont plateau region of the south-eastern states comes to be one of considerable interest, the importance of which will continue to increase as the favorable conditions for manufactures and agriculture in this region will make it in the near future the most thickly populated portion of the South Atlantic states.

Water supplies from surface streams are unqestionably of the first importance; and in the mountain counties where the region is still largely forest covered and the streams rapid and continually aerated by rapids and cascades, the water is of superior purity and clearness. This statement is also applicable to the more elevated and sparsely settled portions of the Piedmont pleateau; but in the less hilly and more thickly settled portions of this region the streams are more sluggish and the waters more muddy and less pure owing to the fact that a much larger proportion of the surface is

* From Trans. Am. Inst. Mining Engineers, XXV., 1895.

under cultivation. Furthermore, many of the towns and manufacturing establishments are located at distances from the larger rivers and creeks too great to permit of the water being lifted and transported to them by pipe lines at any reasonable cost.

Rain water caught from the roofs of houses, under favorable conditions, and kept in properly constructed cisterns, is probably the safest for drinking purposes, but under unfavorable conditions and when not properly attended to, cistern water must be considered as not altogether safe; and in any case the supply is inadequate for large establishments.

Such being the case with regard to surface supplies of water, it will be seen that, in a number of cases, we must depend for potable waters upon underground supplies. These may be obtained either from springs or wells. Of the latter we may consider three varieties: The ordinary open well such as is often seen about private residences; deep bored wells which penetrate the crystalline rocks, in the endeavor to obtain artesian supplies of water; and the shallow bored wells which are put down through the soil to the surface of these crystalline rocks in the hope of striking underground currents along the lines of contract between the lower portion of the soil and the upper portion of the undecomposed rock. In this latter case generally several such wells are bored within a short distance of each other and these are connected by iron pipes, and water is pumped from the various pipes through a common pipe to a common reservoir or tank. This is what is generally known as the tube well system.

The open springs furnish an excellent but limited supply of water for family use; a supply, however, which while it is sufficient for the needs of isolated residences,

it is generally inadequate to meet the demand about towns and manufacturing centers, and futhermore, in such latter cases, and frequently even near isolated country residences, the surface in the neighborhood of the spring becomes so contaminated with decaying organic matter that the water becomes unfit for drinking purposes. The same general statement may be made concerning ordinary open or driven wells, which for the sake of convenience must be located near residences where the surface soil becomes more liable to contamination as the region becomes more thickly settled. Examples of this are not infrequently seen, where the water from wells and springs in newly settled communities is found to be healthful, but a few years later it has become so contaminated with organic matter, which has permeated the soil from above, that sickness follows its use, and it must be finally abandoned. It is difficult, however, to get the average citizen to understand that the organic matter of the water in his well or spring comes from the soil immediately about his premises, as the prevailing notion concerning these supplies of water is that they come, not from the immediate vicinity, but from some distant region. Consequently in many of our towns and even about the isolated country residences, the barn yards and the privies and the hog pens seem to be built upon the principle of convenience alone, and this frequently places them in close proximity to the well or spring from which the family supplies of drinking water are obtained.

But outside of this the question as to the purity of the water, the supply of water from the isolated springs and open wells is generally quite inadequate for towns or manufacturing establishments of any considerable

size unless the number of these wells is greatly multiplied, and their multiplication means their wider distribution through the settlement or community, and thus a multiplication of the possible sources of disease from the drinking of contaminated waters. Nevertheless, the fact remains that, many of the towns of this region, with a population of from a few hundred to several thousand, are still without any general supply of water other than that from independant shallow wells. And while the amount of disease in such cases generally increases with the age of the town, and the physicans, at least, recognize the increasing contamination of the water as the source of this increase in sickness, yet for the lack of a better system this one continues in existence.

Deep artesian well supplies are not to be depended upon for the reason that the geologic conditions in the the Piedmont plateau region are not favorable. The rocks of this region are crystalline schists, gneiss and granites with the dips (schistocity) generally steep and varying on both sides of the vertical. A considerable number of borings varying from 100 to 1000 feet, have been made into these crystalline rocks in the Piedmont region of the two Carolinas and Georgia during the past few years, with the expectation of securing either an "artesian" (overflow) supply, or a supply that would come near enough to the surface to be reached by pumps. But the results have been generally unsatisfactory, the holes being "dry" or the supply of water being inadequate. A somewhat exceptionally favorable result was experienced in Atlanta. Some years ago (1881–82) a well was bored into the gneiss rock in the heart of Atlanta to a depth of about 2200 feet, at a cost of about $20,000.00. At a depth of 1,100

feet a large supply of water was tapped, and it rose to within about 17 feet of the surface. For several years this well constituted the water supply for a considerable part of the city, but the water was pronounced unsafe by the medical authorities, and the well has been abandoned for a water supply from the Chattahooche river. In a few other cases exceptionally large supplies of water have been reached; but as a rule the boring of these wells has failed of satisfactory results.

Some professional well borers, like some professional miners, with a laudable desire to be kept busy, urge that the deeper the hole the better are the chances of success; an opinion that has frequently but slight foundation in the case of the mines, and in the case of well boring it is, in this region of crystalline rocks, contrary to both theory and experience. The possibility of exceptions no one will deny, as we see that in a few of the deeper mines of this region considerable streams of water are tapped; and in some cases there is a bare possibility that the hole to be drilled for a water supply may tap such an underground stream of water, as was the case in Atlanta; but the chances are more than 10 to 1 against such "luck." As a rule these crystalline rocks become harder and more solid as we descend, the chances of securing a reasonable supply of water—never good after the hole enters the real mass of rock—may be said to decrease as the hole descends. There is, however, one certainty about this operation, and that is, other things being equal, the deeper the hole the more rapidily the cost increases.

During the past few years the tube well system mentioned above has been introduced in a number of communities in this piedmont region and with decided success in furnishing a good supply of drinking water

to the smaller towns and manufacturing communities. This system is based upon the existence of fairly well defined underground "currents" of water in regions where the topography is favorable and where the rocks have decayed to a considerable depth, and where near the lower limit of this decay there is more or less porous material through which this water may readily percolate. Of course it has been well known in the past that more or less well defined underground movements of water existed, and that at favorable locations the small currents come to the surface as springs, and that frequently, on both elevated regions and about lowlands, when wells are sunk sufficiently deep into the soil,—usually near the surface of the hard rocks,—a sufficient amount of water is found either to empty into the well as a small stream or to ooze into it from the surrounding soil and thus furnish a limited supply. But it is only recently that the location and extent of these underground sources of water have been investigated in some regions with considerable care and have been found to yield under proper treatment much larger quantities of water than have been reckoned upon in the past. This investigation has been prosecuted in this region mainly by Mr. Henry E. Knox, Jr., a hydraulic engineer, of Charlotte, N. C., and he has in this way located considerable supplies of underground water in regions where these were sorely needed.

I give below, in tabulated form, the results obtained by Mr. Knox in Piedmont North and South Carolina. His method of investigation is to examine carefully the topography and geology of the region where the water supply is needed. The topographic conditions favorable to success are, as might be expected, where there is more or less of the basin, shallow ravine, or valley,

so that the water that falls upon this surface, instead of running off in opposite directions, if the soil is sufficiently porous naturally percolates downward and tends to concentrate along the lower portion of such basin or valley where it may meet with least resistance in the more porous materials.

By way of exploring such a region, a number of holes are bored in line across the basin or valley, so as to determine the existence and location of such an underground "current" of water. In this way its position at intervals is determined and the intervening course is traced by additional borings. If the water supply is tapped by these borings it sometimes overflows; the output of the pipe at the surface of the ground and the quantity thus overflowing is measured, and pumps are then applied so that the possible yield of water can be estimated. In these underground 'streams' the water usually follows the topographic conditions, as might be expected, but in some cases it moves more or less obliquely across the ravines, showing that the overlying soil has not the same thickness everywhere, and that the topography of the soil surface is not the same as the topography of the underlying rock surface; and the water current moves along down the incline of least resistance of the rock surface, in a measure independently of the topography of the surface soil.

The fact that that the water percolates through this more or less porous material at considerable depths below the surface, of course suggests that the movement must be sluggish; but that there is a definite movement is shown by the fact that where there are a number of holes bored at intervals along the line of the "stream" and coloring matters are introduced into one of them, in a short time the color ap-

pears in the water coming from the adjacent holes in one direction but does not appear in the water from the holes in the opposite direction. But the average rate of movement has not been determined with a sufficient degree of accuracy to admit of its being stated. These currents are quite limited in their width; ranging in the cases tested, from a few feet to, in rare cases, more than 100 yards. And, as might be expected, the width is not at all constant, but while it gradually increases further down the "stream" as the supply of water becomes greater, yet this increase of width is by no means constant. The depth at which these underground water currents have been found varies from about 20 to nearly 100 feet, and generally they have been found at less than 50 feet below the surface.

The fact that in the case of some of these wells the water overflows at the surface is due to topographic rather than geologic influences. In some cases, especially at Charlotte, N. C., as mentioned in the table below, the flow from a single well amounts to as much as 10 gallons per minute. Here, as in other places where the overflow is slight—even less than one gallon per minute—the amount of water which can be pumped from such a well is considerably larger. Thus in the case mentioned at Charlotte (Latta Park) there are several overflowing wells with an average depth of 42 feet. The maximum natural flow from one of these wells is 10 gallons per minute, but with the application of a pump the eight wells yield readily 230,000 gallons per day. Again at Chester, S. C., one well which yields in natural overflow 6 gallons per minute, with the aid of a pump yields nearly 62 gallons per minute or 99,280 gallons per day. In another case, the maximum natural overflow of any one of the eight wells

bored at the Western Hospital, at Morganton, N. C., is only four gallons per minute, while the eight wells, with an average depth of about 39 feet, yield upon the application of a pump 165 gallons per minute or 237,600 gallons per day.

The quality of the water obtained from these wells has been pronounced satisfactory in every case by the health officials. Of course the continuation of this condition of things will depend largely upon the continued freedom from contaminating influences of these water basins, and one advantage of this system of water supply is that the basins, being generally limited in area, may be generally controlled by one or more individuals or a corporation, and may be thus kept free from sources of contamination.

As might be expected, the search for the underground supplies of water has not by any means been successful in every case, but the limited experience leads one to believe that they may be found in a majority of communities, where search is extended over a sufficiently large area and is made with sufficient care. It would at present, however, be too much to claim that these underground supplies of drinking water can be found sufficient to meet all the demands of larger towns and cities, though they would prove of material service in this connection. But I anticipate that they will be found of greatest importance in connection with water supplies of smaller towns and of more or less isolated manufacturing establishments, where there are usually several hundred or several thousand operatives.

In the following tabular statement will be found a list of the more important places where these underground water currents have been found and where the gang well system has been introduced, the name of the

special establishments for which the wells were bored, the number of wells at each place, the average depth of the wells, the natural overflow in one minute of time from that one of the series of wells from which the overflow is largest, and the aggregate yield of wa- from the several wells at each place in 24 hours when the steam pump is applied. The data for this tabular statement has been supplied by Mr. Henry E. Knox Jr., of Charlotte, N. C., who bored all of these wells. and who states that out of 23 surveys made by him, only three were unsuccessful in locating the desired quantity and quality of water.

LIST OF FLOWING WELLS IN THE PIEDMONT PLATEAU REGION OF NORTH AND SOUTH CAROLINA.

BORED BY HENRY E. KNOX, JR., HYDRAULIC ENGINEER, CHARLOTTE, N. C.

PLACE.	Av'rge Depth in feet	Strata.	No. of wells.	Max. flow per minute from one well.	Pumping capacity 24 hours.	For whom bored
Burlington, N. C.	27.5	Bed of gravel.	5	1 Gallon.	20,000 Gals.	Aurora Cotton Mills.
Morganton, "	28.3	Decom. gneiss	8	1 "	150,000 "	Burke Tanning Co.
"	39.0	" "	8	4 "	237,600 "	State Hospital.
"	41.0	" "	5	1 "	100,000 "	Deaf and Dumb School.
Rock Hill, S. C.	56.0	" granite	4	5 "	72,000 "	Winthrop N. and I. College.
Fort Mill, "	35.0	" "	4	5 "	30,000 "	Fort Mill Man'f. Co.
Pelzer, "	21.0	" gneiss	4	10 "	100,000 "	Pelzer " "
"	38.0	" "	5	1 "	100,000 "	" " "
Chester, "	40.3	" granite	1	6 "	99,280 "	Gingham Mills.
"	42.5	" "	1	2 "	30,000 "	" "
"	72.0	" "	2	1 "	30,000 "	Catawba "
Charlotte, N. C.	42.0	" "	10	10 "	230,000 "	E. D. Latta.
"	51.5	" "	10	2½ "	200,000 "	Water Works Co.
Jonesboro, "	31.0	" schist	1	1½ "	5,000 "	Jonesboro Cotton Mills.
Reidsville, "	28.0	" granite	10	1 "	100,000 "	Edna Cotton Mills.